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DIAGNOSTICS AND CHEMICAL APPLICATIONS OF MULTIPHOTON ABSORPTION--ETC(U)
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FINAL SCIENTIFIC REPORT

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"DIAGNOSTICS AND CHEMICAL APPLICATIONS OF
MULTIPHOTON ABSORPTION PROCESSES"

by

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1 April 1977 - 30 September 1981

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I. Objective

To examine and analyze quantitatively the mechanism and parameters of the processes of multiphoton absorption from intense laser fields and to observe and measure the intramolecular dynamic processes following such absorption.

II. Method

It was the original objective of the present program to develop a simple molecular beam system for examining the effect of various laser parameters on the rate of energy absorption by irradiated molecules. In the course of developing this system we discovered the utility of using isotopic branching to accomplish a similar purpose and to that end we have explored the multiphoton dissociation of 2-deuterioethyl chloride, CH_2DCH_2Cl (C_2H_4DCl).

Excitation of C_2H_4DCl above the activation threshold of about 56 kcal leads to production of HCl or DCl in a concerted molecular process:

$$C_2H_4DCl \xrightarrow[\text{or}\Delta]{nh\nu} C_2H_4DCl^* \begin{cases} \xrightarrow{1} CHD = CH_2 + HCl \\ \xrightarrow{1'} C_2H_4 + DCl \end{cases}$$

The branching ratio $R = k_1/k_1'$ can be measured from the final products and is a monotonic function of the energy of the decomposing molecules. We have made a careful study [ref.5] of the thermal system from 700 - 1000°K and find the Arrhenius relation:

$$k_1/k_1' = 1.44\ (\pm\ 0.05)\ \exp\left\{(1500\ (\pm 50\ \text{cal/mol°K})/RT\right\}$$

We have also modeled the system (RRKM Theory) and shown that the model fits the absolute rates in the pressure dependent region. This

permits us to assign a mean energy content E to each value of R observed and to fix the mean time of decomposition of the decomposing molecule 3,5 [Ref. ~~3,4,~~6]. In this way the observes branching ratio provides a "chemical clock" for the last excitation and decomposition events. At low pressures (< 100 mtorr, $t_{collision} \geq 10^{-5.5}$sec) the average decomposing molecule had an internal energy of 88 ± 6 kcal and decomposed in $10^{-9 \pm 0.5}$ sec. It thus absorbed its <u>last</u> photon in about 1 to 3 nanoseconds.

On studying the effects of pressure 2,4,5 [Ref. ~~2,5,~~6] on this system we discovered the bimodal response to the laser pulse shape. A typical laser pulse has an intense; short peak (0.1μsec) and a long, weaker tail (∿1μsec) each with about 1/2 the total energy. Each pumps at a different rate and produces a different energy population. At 30 torr Ne (or He) we see only the effects of the short peak, the slowly pumped molecules in the tail being quenched by collisions before dissociation. The branching ratio R_p corresponding to this peak have energies of 130 ± 15 kcal/mole and life-times of about $10^{-11 \pm 0.5}$ sec. They absorbed their last photon in 10^{-11} sec and have experienced pumping and decomposition in a single mode pulse during a time of about 5 nanosec. To do this the energized molecule had to have an absorption cross-section about 100 times larger than the cross-section of room temperature molecules.

We feel that the discovery of isotopic branching as a chemical clock provides an important new tool to laser scientists. It makes it possible to place intramolecular laser events on an absolute time scale and to begin to ask and answer questions about the time scale for the flow of energy in molecules, both large (> 6 atoms) and very large.

MAJOR ACHIEVEMENTS

(A) Establishment of isotope branching as chemical clock and energy measure via RRKM

(B) Connection of Thermal—Fall-off and RRKM with MPD via RRKM

(C) Discovery of huge changes in X-section with energy

(D) Discovery of peak and tail effects

(E) Operations of molecular beam with pulse inlet and IR and excimer laser irradiation

ACTIVE PERSONNEL

1.) Dr. A. J. Colussi
2.) Dr. J. C. Diels
3.) Dr. P. J. Evans
4.) Dr. P. Papagiannakopoulos
5.) Professor Choi (Korea)
6.) Mr. Ken Kosnik (grad student)

PUBLICATIONS

1.) "Molecular Beam Sampling", A. J. Colussi and Sidney W. Benson, Int. J. Chem. Kin. 10, 1091 (1978).

2.) "Intramolecular Isotope Effects in Laser Multiphoton Dissociation of CH_2DCH_2Cl, A. J. Colussi, R. J. Hwang, J. Tiee and Sidney W. Benson, Chem. Phys. Letters, 52, 349 (1977).

3.) "The Prediction of Thermochemical and Kinetic Data for Gas Phase Reactions". (Plenary Lecture). 4th Int. Symp. on Plasma Chemistry, S. W. Benson, Pure and Applied Chem., 52, 1767 (1980).

4.) "Intramolecular Isotopic Effect in the Pyrolysis of Ethyl-2d_1 Chloride, P. J. Papagiannakopoulos and Sidney W. Benson, Int. J. Chem. Kin. (1982).

5.) "The Effects of Buffer Gases in the Infrared Multiphoton Dissociation of C_2H_4DCl. A Chemical Clock to Explore Highly Excited Molecules", P. J. Papagiannakopoulos, Ken Kosnik and Sidney W. Benson, Int. J. Chem. Kin. (1982).

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Laser - deutero ethyl chloride, isotope effects collisional quenching

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Isotopic branching ratios are shown to be a very sensitive tool for the quantitative analysis of the absolute time scale and total energy content of molecules undergoing photolysis in an IR laser beam. A study and RRKM analysis has been done of the thermal decomposition of deutero-ethyl chloride over the range 700-1100°K and at high and low pressures (fall-off region). This has been applied to analysis of the multiphoton dissociation with a CO_2 laser at varying pressures. It is shown that the laser pulse produces two independent effects due to its long, low intensity tail following the high intensity peak. In the latter

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molecules absorb about 85 kcal and decompose in $10^{-8.5}$ sec. Also of importance is the finding that energized molecules can have IR absorption cross-sections an order of magnitude or more greater than their cross-section at room temperature.

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